



Research and Development

Emissions of Air Toxics from a

Simulated Charcoal Kiln

Equipped with an Afterburner

Prepared for

EPA Region 7

Prepared by

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FOREWORD

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Final Report

**Emissions of Air Toxics from a Simulated Charcoal Kiln
Equipped with an Afterburner**

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ABSTRACT

A laboratory-scale simulator was constructed and tested to determine if it could be used to produce charcoal that was similar to the charcoal that is produced in Missouri-type charcoal kilns. An afterburner was added later to study conditions for oxidizing the volatile organic compounds contained in the combustion gases that are produced when wood is converted to charcoal. Five burns were conducted to shake down the operation of the afterburner; then four full burns were completed to measure the effectiveness of the afterburner. Based on these simplified studies on the effect of an afterburner on emissions from Missouri-type charcoal kilns, it appears that, while the afterburner can offer significant benefits under some conditions, the operation of the afterburner is not a trivial matter. A system such as a charcoal kiln, that relies on natural draft for operation, may be upset by the addition of an afterburner due to pressure changes in the stack that influence the natural draft. Optimizing the process, both in the sense of good charcoal quality and good afterburner performance, may be difficult without the benefit of continuous emission monitors.

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1.0 INTRODUCTION

A “Missouri-type” charcoal kiln is a small (usually about 40 feet wide, 60 feet long, and 16 feet high) building often constructed with brick, cement, or metal that is used to burn wood with a limited supply of air to produce charcoal. The U.S. Environmental Protection Agency (EPA), National Risk Management Research Laboratory (NRMRL), Air Pollution Prevention and Control Division (APPCD) agreed to provide EPA Region 7 Air, Resource Conservation and Recovery Act (RCRA), and Toxics Division (ARTD) with chemical and physical information to characterize the plumes from Missouri-type charcoal kilns. That work was completed as planned [Lemieux, 1999] and resulted in several important conclusions, some of which were:

- Charcoal could be produced in the laboratory kiln simulator. The charcoal produced in the simulator was identical to the charcoal produced in Missouri-type kilns according to all characteristic measurements performed on the two charcoals.
- The simulated charcoal kiln produced combustion gases containing significant amounts of volatile and semivolatile organic compounds. Benzene was found in the combustion gases at concentrations approaching 2000 ppmv.
- Many oxygenated organic compounds were found in the combustion gases from the simulated charcoal kiln.
- Several polycyclic aromatic hydrocarbons (PAHs) were found in the simulated charcoal kiln combustion gases.

As the earlier [Lemieux, 1999] experiments were being conducted, Region 7 requested that an additional research study be conducted by APPCD during fiscal year 1998 to obtain information on the effectiveness of adding afterburners to these kinds of charcoal kilns.

The objectives of this work were:

- To install an afterburner onto the simulator used in the earlier [Lemieux, 1999] experiments and evaluate its performance.
- To produce charcoal that was representative of the charcoal produced in Missouri-type charcoal kilns while using the afterburner.
- To install a larger dilution tunnel capable of greater dilution ratios and more representative samples of condensable organic matter and particulate.
- To improve the seals in the kiln simulator to minimize unknown sources of air in-leakage.

- To determine the concentrations of several pollutants that were not measured in the earlier [Lemieux, 1999] tests in the combustion gases generated as the wood was converted into charcoal.
- To determine if any of those pollutants could be destroyed by passing them through an afterburner inserted into the exit duct from the simulated charcoal kiln.

Variables that were measured on a continuous basis included the weight of the kiln, the temperature at various places inside the simulator, and the concentrations of carbon monoxide (CO), carbon dioxide (CO₂), nitric oxide (NO), total hydrocarbons (THCs), and oxygen (O₂) in the combustion gases as the gases exited the afterburner. This set of variables is referred to collectively in this document as the “continuous measurement variables.” Nine experiments were performed altogether. Five experiments (Runs A through E) were performed to optimize the operating conditions of the kiln and the afterburner. Four additional experiments (Runs 1 through 4) were performed while additional data were obtained by analyzing extractive samples for volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), aldehydes, and particulate matter (PM), with two of the four runs being performed with the afterburner switched off and two runs being made with the afterburner switched on. An additional blank experiment was performed to assess system contamination.

2.0 EXPERIMENTAL METHODS

2.1 Experimental Facility

The tests were conducted at APPCD's Open Burning Test Facility (OBTF). For these tests, a charcoal kiln simulator, constructed based on guidance from ARTD, APPCD, and published literature, was the experimental device used to simulate full-scale charcoal kilns. The kiln was constructed to hold approximately 35 pounds of dried oak wood. A schematic of the test setup and details of the kiln simulator are shown in Figure 2-1. The kiln geometry and configuration were similar to representative full-scale commercial units, and the unit was sized to be positioned on a weigh scale to record weight loss data continuously.

A small afterburner was installed in the exit duct leading from the kiln. Initially a small pilot burner (see Figure 2-2) was used, but the distribution of the flame in the duct was found to be not uniform enough to provide a stable secondary combustion environment. After the August 28, 1998, test, a perforated metal plate (see Figure 2-3) was installed to aid in the distribution of the flame across the duct.

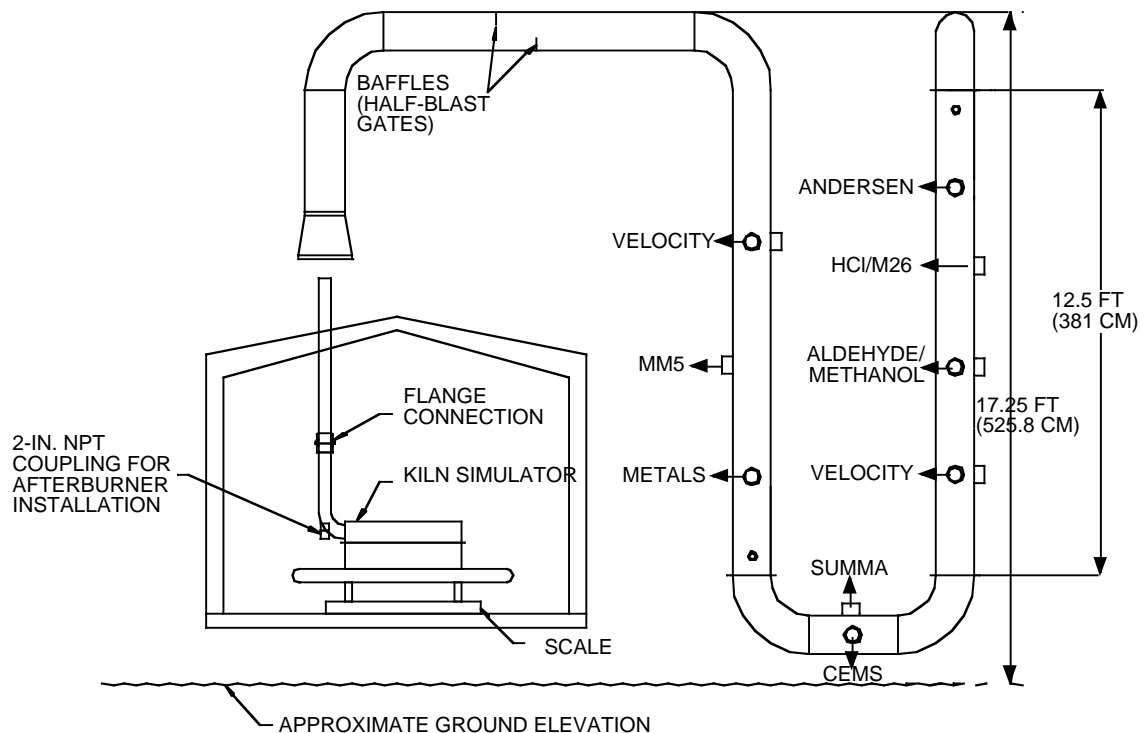


Figure 2-1. Open Burning Test Facility Setup for Charcoal Kiln Emissions Studies



Figure 2-2. Photograph of Afterburner



Figure 2-3. Perforated Metal Distribution Plate

Air was introduced into the kiln two ways: 1) through a series of side ports that could be capped off; and 2) through a series of pipes mounted along the outside of the kiln. Figure 2-4 is a perspective view of the kiln with the various inlet ports. It was found that the afterburner exerted a back pressure on the system, so the air flow into the kiln simulator was provided using a forced air fan. The air inlet ports provided metered air flow into the kiln. The metering of the air was designed so as not to impact operation of the system and to simulate the air influx due to natural draft. Full-scale kilns typically use manually activated dampers and natural draft to control air flow. Note that the back pressure that the afterburner imposed onto the natural draft, that provided the main flow of the air into the kiln during each run, was significant for the kiln simulator. It is not known whether

this effect would be significant in a full-scale kiln, but it should be considered a possibility.

Twenty thermocouple ports along the walls of the kiln simulator were used to profile the temperature within the chamber, although not all thermocouple ports were occupied by thermocouples. By observing the local temperature measurements, hot/cold spots within the chamber were located and air flow to the corresponding air inlet port was adjusted to maintain uniform conditions. Full-scale kilns typically have no temperature monitoring capabilities, and exhibit significant thermal gradients from one end of the kiln to the other as the flame front propagates through the mass of wood inside. Figure 2-5 shows the locations of the thermocouples in terms of the number of each thermocouple's corresponding channel on the data acquisition system.

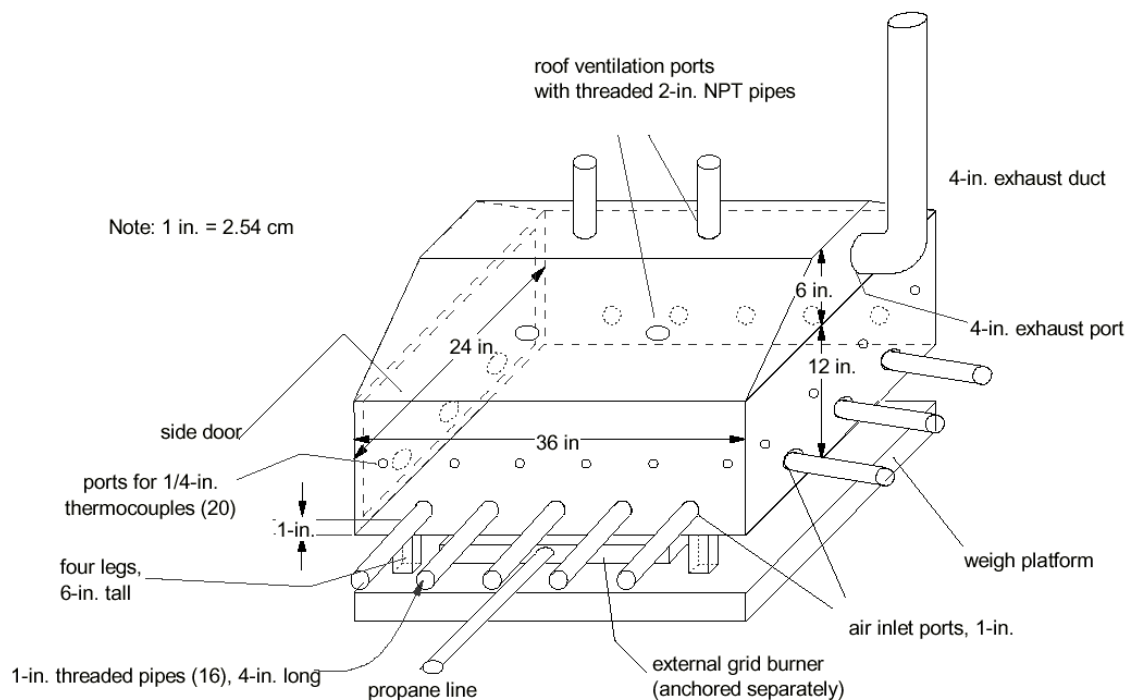


Figure 2-4. Perspective View of the Charcoal Kiln Simulator

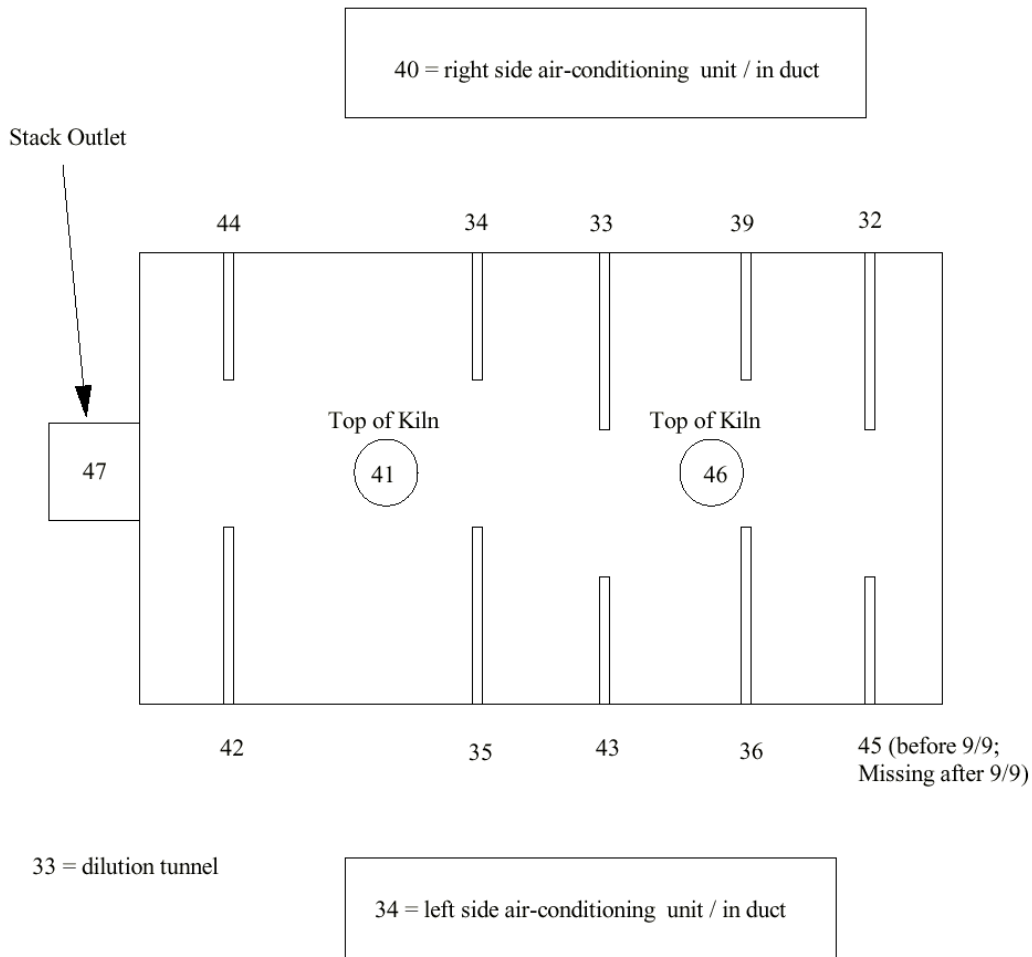


Figure 2-5. Thermocouple Locations and Identification

2.2 Run Procedures

For each run, the side ports were opened and a hand-held propane torch was used to ignite the wood in the kiln. After a period of time, when the combustion of the wood was stabilized, the side ports were closed and the only flow of air into the kiln was through the metered forced-air inlet ports. The flow rate of the air through those ports was measured continuously throughout the test, and was occasionally adjusted based on the operator's experience making acceptable quality charcoal. Table 2-1 lists the various runs and flow rates as well as information about the opening of the various ports as a function of run time.

Note that the weight measurements were sometimes perturbed when the wood was lit by the propane torch. Also note that, where a visual observation of the flames or coals within the kiln was made (as opposed to a smoke observation), it is also possible, although not likely, that the weight measurements may be perturbed. These periods of observation were brief and not routinely performed due to the intense heat within the facility.

Table 2-1. Timelines of Runs

Run	Description	Date	Time	# of Ports Open	Kiln Input Forced Air Flow (L/min)	AB Propane (L/hr)	AB Air (L/hr)
A	1 st AB Scoping Test	8/21/98	1505	3	0	0	0
			1519	3	0	56.6	56.6
			1540	3	0	0	0
			1557	0	0	0	0
			1423	0	0	113.3	56.6
			1640	0	0	0	0
B	2 nd AB Scoping Test	8/25/98	1059	3	0	0	1133
			1121	3	0	113.3	1133
			1148	0	0	0	1133
			1216	0	0	113.3	1133
			1242	0	0	0	1133
			1258	0	0	113.3	1133
			1318	0	0	0	1133
C	3 rd AB Scoping Test; added distribution plate to burner	8/28/98	0958	3	0	0	1472
			1042	3	113.3	0	1472
			1051	3	113.3	113.3	1472
			1107	3	113.3	0	1472
			1125	0	0	0	1472
			1138	0	0	113.3	1472
			1148	0	0	0	1472
			1218	0	0	113.3	1472
D	4 th AB Scoping Test	9/2/98	1238	0	0	0	1472
			1407	3	169.9	0	2124
			1410	3	226.5	0	2124
			1420	3	113.3	0	2124
			1429	3	113.3	56.6	2124
			1442	3	113.3	0	2124
			1503	0	113.3	0	2124
			1512	0	113.3	85.0	2124
			1523	0	113.3	0	2124
			1535	0	113.3	113.3	2124
			1549	0	113.3	0	2124
			1558	0	113.3	113.3	1076
			1606	0	113.3	113.3	566.3
			1611	0	113.3	368.1	424.8
			1616	0	113.3	0	424.8
			1620	0	113.3	0	2124
			1639	0	113.3	113.3	1133
			1647	0	113.3	0	1133

(continued)

Table 2-1 (continued). Timelines of Runs.

Run	Description	Date	Time	# of Ports Open	Kiln Input Forced Air Flow (L/min)	AB Propane (L/hr)	AB Air (L/hr)
E	5 th AB Scoping Test; cycling of AB	9/3/98	1252	3	237.9	0	4446
			1305	3	237.9	0	2209
			1317	3	237.9	0	4644
			1327	3	237.9	113.3	4106
			1340	3	237.9	0	4106
			1351	0	141.6	0	4106
			1359	0	141.6	113.3	3398
			1408	0	141.6	283.2	3398
			1412	0	141.6	0	3398
			1426	0	141.6	113.3	1982
			1434	0	141.6	113.3	3540
			1442	0	141.6	0	3540
			1451	0	141.6	141.6	2124
			1459	0	141.6	85.0	3540
			1504	0	141.6	226.5	3540
			1506	0	141.6	141.6	2124
			1513	0	141.6	0	2124
1	1 st Full Test; AB Off	9/10/98	1318	3	240.7	0	0
			1410	0	240.7	0	0
			1518	0	0	0	0
2	2 nd Full Test; AB On	9/14/98	1505	2	237.9	113.3	1982
			1600	0	85.0	113.3	1982
			1626	0	0	113.3	1982
3	3 rd Full Test; AB On	9/16/98	1308	3	181.2	113.3	3483
			1411	0	99.1	113.3	3455
			1421	0	0	113.3	3455
			1553	0	0	113.3	3228
4	4 th Full Test; AB Off	9/18/98	1147	3	169.9	0	0
			1251	0	85.0	0	0
			1301	0	0	0	0

Unless otherwise noted, assume that the standard afterburner procedure was to leave the additional afterburner air on throughout the test. The electric ignitor and propane would be switched on at various times. Also assume that the ignitor was always activated when the propane was initially switched on, and generally switched off after a short period once the afterburner flame was self-sustaining.

2.3 Sampling and Analytical Procedures

Continuous emission monitors (CEMs) were used to measure CO, CO₂, NO, O₂, and THC_s as described in the earlier work [Lemieux, 1999]. Quality control data (Appendix A) indicate that this arrangement produced reliable data.

VOCs were collected in 6-liter stainless steel SUMMA® canisters and were analyzed by EPA Method TO-14 using gas chromatography for the mixture separation and mass spectrometry detection and quantification of each of the separated compounds [Winberry, et al., 1988].

Methanol sampling and analysis were conducted using Method 308 [U.S. Government Printing Office, 1977-1982].

Aldehydes were sampled and analyzed using Method IP-6A [Winberry et al., 1990].

Semivolatile sampling was performed using EPA Method 0010 [U.S. EPA, 1986a]. The samples were extracted and analyzed by EPA Method 8270C [U.S. EPA, 1986b]. Total PM was measured using an EPA Method 5/Method 26 train. PM measurements do not include condensables. Although a dilution tunnel system reminiscent of Method 5G was used, it would not be accurate to use Method 5G to describe the PM sampling for two reasons: 1) Method 5G uses two filters in series, whereas Method 5 uses only one; we used one; and 2) Method 5G limits the temperature of the “hot box” filter holder to a lower temperature than is used in Method 5; our “hot box” operation was compliant with Method 5.

Additional PM sampling was conducted in the dilution tunnel, with particle size measurements accomplished with Andersen impactors [Harris, 1977].

2.4 Calculations

The estimated emissions of each pollutant were calculated using Equation (1).

$$E = (C_{\text{sample}} Q_{\text{DT}} t_{\text{run}}) / (m_{\text{fed}}) \quad (1)$$

Where

E = estimated emissions of the pollutant [g/kg wood fed]

C_{sample} = concentration of the pollutant in the dilution tunnel [g/m³]

Q_{DT} = flow rate of gas in the dilution tunnel [m^3/min]

t_{run} = sampling time [min]

m_{fed} = mass of wood fed to the kiln [kg]

3.0 RESULTS

3.1 Temperature Profile During a Burn

Figure 3-1 is an example of a graph showing the temperature at one of the locations inside the kiln as a function of time during a burn. The temperature rose sharply as the fire became established, reached a maximum of about 650-750 °C, and then slowly decreased as the supply of O₂ was decreased and the rate of combustion was reduced. Qualitatively, the temperature profiles of all of the burns had the same general shape. There was considerably more scatter between the sensors at the different locations inside the simulator for some burns than for others.

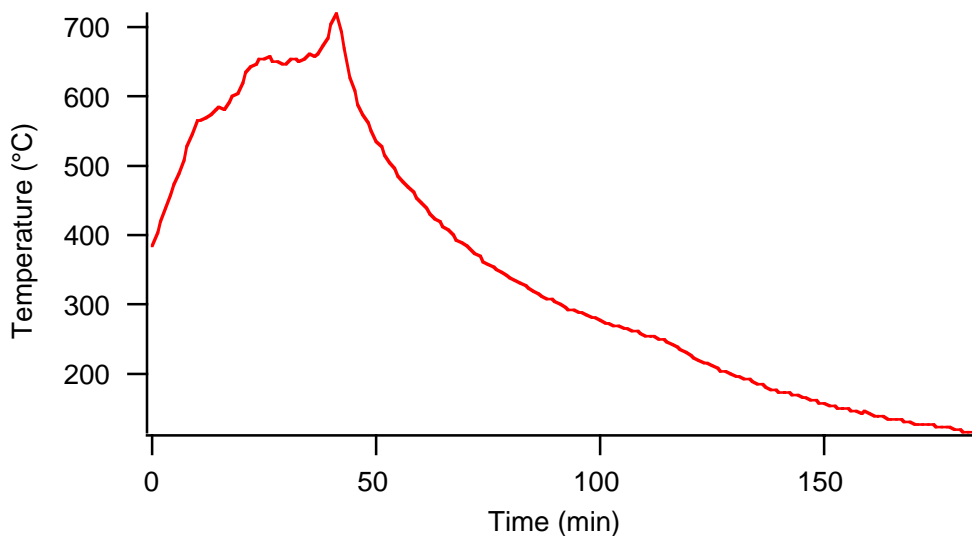


Figure 3-1. Typical Profile of the Temperature Inside the Simulator (TC 47) as a Function of Time Into a Burn from Run 1.

3.2 Weight Profile During a Burn

Figure 3-2 is a typical example showing the changes in the weight of the simulator, associated equipment, and the remaining wood, ashes, etc. as a function of the time into the burn. For most burns, the final weight of the charcoal was measured well within the expected range of 20-30% of the weight of the wood that was fed, although in Run 1, all but 6% of the original wood was consumed, and in Run 4, 42% of the original wood remained; those two tests did not produce acceptable charcoal.

Because of weigh scale problems exhibited with accuracy of online measurements, an independent measurement of the weight of the initial wood and charcoal was used for calculation of the estimated emissions.

For the five system optimization burns performed during the time period of August 21-September 3rd, the afterburner was switched on and off one or more times during each run. For the four experimental burns completed on September 10-18, the afterburner was left on or off for the entire burn. Table 3-1 summarizes the data for the nine experiments. As with previous work, the data indicate that most burns are consistent in that the kiln temperature is approximately the same inside the kiln and that the wood is converted into charcoal in a more-or-less uniform manner.

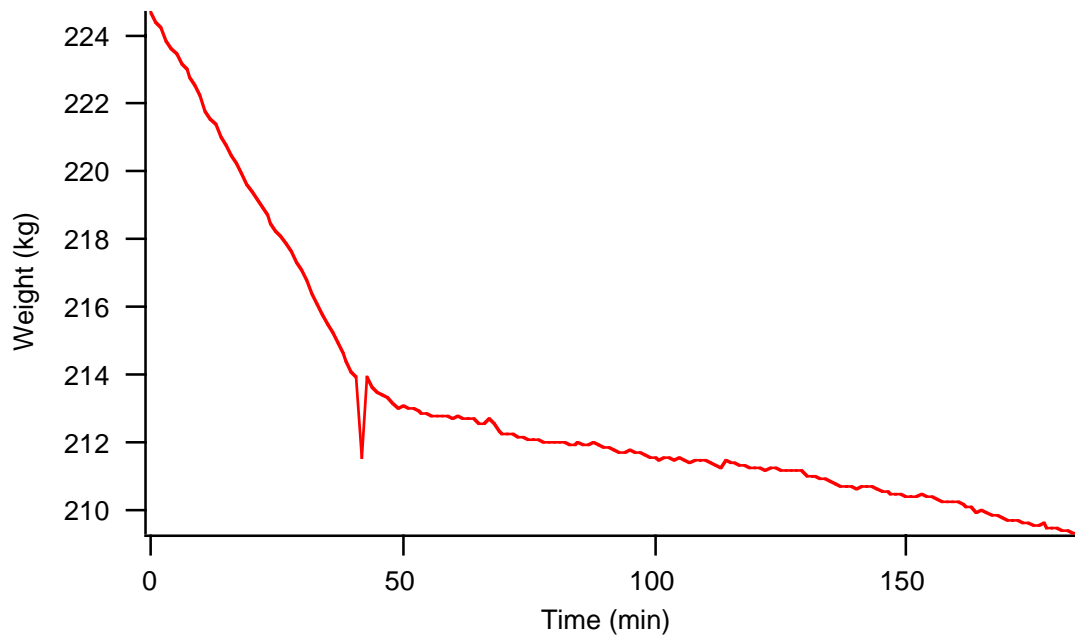


Figure 3-2. Example of a Weight Profile as a Function of Time Into Run 1.

Table 3-1. Summary of the Physical Data for the Nine Runs

Run	Description	Max. Temp. (°C)	Initial Wood Weight (kg)	Charcoal Weight (kg)	Charcoal/ Wood Ratio
Shakedown Runs					
A	1 st AB	750	14.5*	3.2	0.22
B	2 nd AB	750	15.7	4.6	0.29
C	3 rd AB	650	22.7	15.6	0.69
D	4 th AB	700	14.5*	11.8	0.82
E	Cycle AB	625	14.7	3.6	0.24
Runs with Extractive Sampling					
1	AB Off	715	14.3	0.8	0.06
2	AB On	625	14.5*	3.5	0.24
3	AB On	700	13.1	4.0	0.31
4	AB Off	625	15.6	6.5	0.42

* - estimated

3.3 Profiles of Combustion Gases During a Burn

Figure 3-3 is an example of the burn profiles for two (O_2 and CO_2) of the combustion gases. Generally, soon after the fire was established, the concentration of O_2 decreased and the concentrations of the oxidation products increased. Table 3-2 summarizes the resulting data. Based on the estimated dilution ratio from the average CO measurements over a representative time, where both the CO pre- and post-dilution measurements were significantly above zero, and from the pitot traverse of the dilution tunnel, the average gas flow rate through the simulator can be estimated. Table 3-3 includes these measurements and estimates. The charcoal kiln flow rate was estimated by dividing the measured flow rate in the dilution tunnel by the calculated dilution ratio.

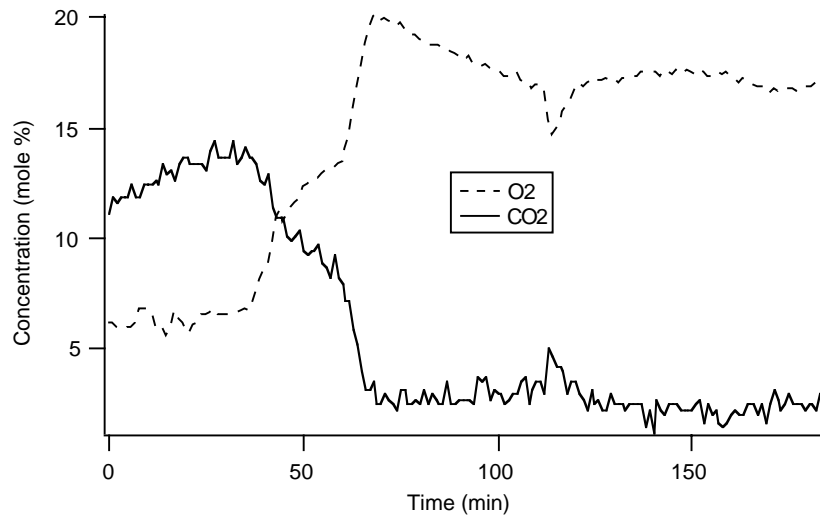


Figure 3-3. Typical Combustion Gas Kiln Burn Profiles from Run 1.

Table 3-2. Combustion Gas Burn Data

Run	O_2 Min. (%)	CO_2 Max. (%)	CO Max. (%)	NO Max. (ppm)*	THC Max. (ppm)*
A	8	6.5	1.2	79	>5000
B	4	7	2.3	NA	5000
C	8	6	0.03	NA	5000
D	3.5	15	2.8	105	>5500
E	3.5	15	3.5	75	>5000
1	6	13	4.3	72	4200
2	6	13	4.2	75	>5000
3	7	10	1	130	5000
4	12	5	0.7	62	4350

NA – not available

* - as measured prior to dilution

Table 3-3. Charcoal Kiln Simulator Flow Estimates

Run	CO Pre-dilution (ppm)*	CO Post-dilution (ppm)*	Dilution Ratio	Dilution Tunnel Flow Rate (m ³ /min)	Est. Charcoal Kiln Gas Flow Rate (m ³ /min)
1	27160	1583	17:1	19.3	1.13
2	15623	1447	11:1	19.3	1.79
3	6194	701	9:1	19.3	2.19
4	684	94	7:1	19.3	2.67

* - note that the average CO measurements were averaged over 20 minute time intervals early in the run where both the pre- and post-dilution CO values were significantly above zero.

3.4 Effect of Cycling Afterburner

Optimization of the afterburner operation was difficult, given the limited time available with which to work. The afterburner exerted a back pressure on the kiln which required supplementing the natural draft with forced air. The system was also sensitive to upsets from ignition of the afterburner during the early part of the run. In a real charcoal kiln, this may not be as much of a problem because the total batch production time is on the order of days whereas in the simulator it was on the order of hours.

However, once some experience was gained in the operation of the afterburner and in balancing the flow rates and pressure, some time still remained in the run in which to examine the effect of the afterburner on the continuous measurements by cycling the afterburner on and off over a period of time.

Figure 3-4 illustrates the CO, CO₂, NO, and THC measurements taken during Run E while the afterburner was being cycled on and off. It is apparent that the afterburner has the potential to significantly reduce CO and THC emissions when it is operated in such a way as to not interfere with the charcoal production process.

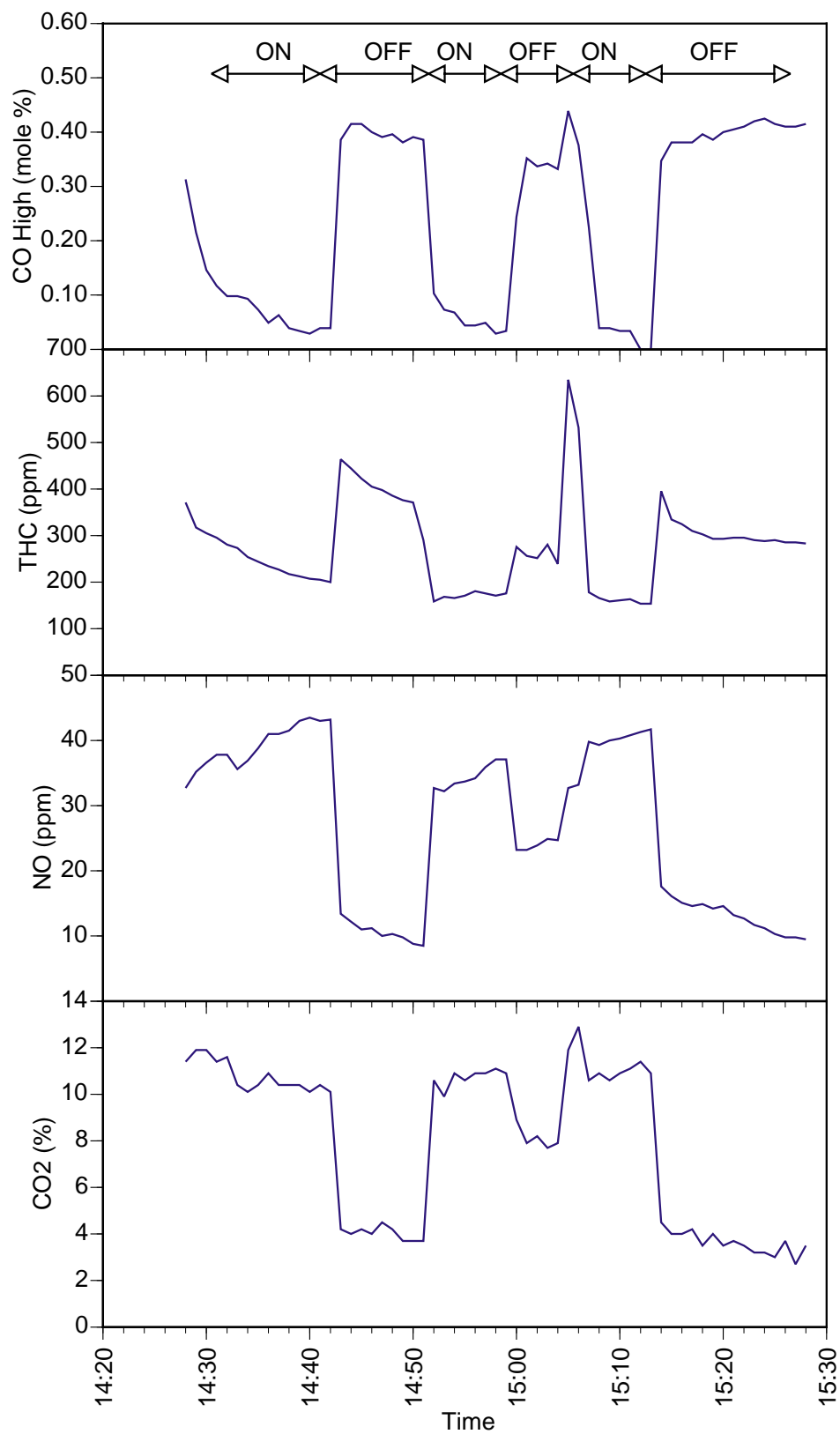


Figure 3-4. Effect of Cycling Afterburner On and Off During Run E.

3.5 Total Particulate Measurements

The total particulate measurements are listed in Table 3-4. Note that PM measurements do not include condensables. Based on these data, the afterburner does not appear to be dramatically effective at reducing PM emissions. However, maintaining stable conditions in the kiln simulator was difficult when the afterburner was running, so these data are not conclusive. Note that Runs 1 and 4 did not exhibit charcoal/wood ratios within the desired 20-30 % range (see Table 3-1). If the PM data from the 1999 report are compared to Runs 2 and 3, it appears that PM emissions are 50-75% lower with the afterburner switched on.

Table 3-4. Total Particulate Measurements

Run	Afterburner	Total PM (g/kg initial wood)
1	off	7.00
2	on	3.42
3	on	1.65
4	off	1.78

3.6 Particle Size Distributions

Table 3-5 lists the particle size distribution data. Figure 3-5 depicts the particle size distributions from the four tests. It appears that the first test on September 10 yielded a significant amount of the mass as submicron particulate; however, there was little to distinguish the results from the other three tests. There was no observable improvement made by operating the afterburner; however, as noted before, the charcoal kiln was not operating in a stable manner when the afterburner was active.

Table 3-5 Particle Size Distribution Data (Mass %)

Aerodynamic Diameter (μm)	Run 1	Run 2	Run 3	Run 4
>12.5	18.1	21.1	39.8	18.4
7.9-12.5	-2.9	5.4	9.3	48.3
5.4-7.8	2.9	9.5	5.3	8.4
3.7-5.3	-0.8	10.2	4.4	6.3
2.4-3.6	-5.3	7.5	21.2	7.7
1.2-2.3	1.9	9.5	6.6	5.9
0.71-1.1	5.1	6.1	-1.8	5.2
0.1-0.70	6.4	5.4	8.0	1.4
< 0.1	73.9	25.2	7.1	-1.6

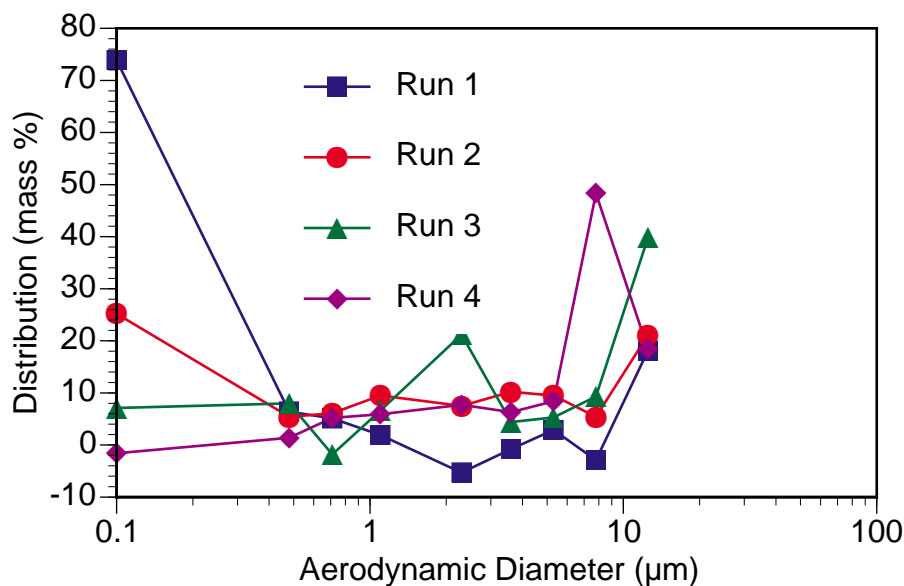


Figure 3-5. Particle Size Distributions.

3.7 Volatile Organic Measurements

Table 3-6 lists the measured VOCs from Runs 1 through 4. No observable difference could be discerned between the runs. Run 4 in particular showed much lower VOCs than the other three runs. Noting that the ratio of charcoal to wood for Run 4 suggested less conversion of wood to charcoal than the other three runs, it may be that more complete quenching occurred in that particular run that limited the emissions of VOCs.

Table 3-6. Volatile Organic Compound Emissions (g/kg initial wood)

Run	1		2		3		4	
Chloromethane	6.22E-01	J,B	8.92E-03	J	1.69E-02		8.31E-03	J
Chloroethane	1.90E-01	J	ND		ND		ND	
1,2-Dichloroethane	ND		4.22E-02		1.42E-02	J	ND	
Benzene	3.95E+00		2.77E+00		5.45E-01		1.05E-02	J
Toluene	5.18E-01	J,B	2.82E-01		6.55E-02	J	ND	
Ethyl benzene	ND		1.65E-02	J	ND		ND	
m,p-Xylenes	4.26E-01	J	8.26E-03	J	ND		ND	
Styrene	ND		2.84E-02	J	5.14E-02	J	ND	
1,4-Dichlorobenzene	2.55E-01	J	ND		ND		1.11E-02	J,B
1,2-Dichlorobenzene	3.98E-01	J	ND		ND		1.50E-02	J,B

ND – not detected; J – Peak below calibration range; B – Found in Blanks

3.8 Semivolatile Organic Measurements

Table 3-7 shows the semivolatile organics, in terms of grams emitted per kilogram of initial wood. Test 1's numbers give good agreement with the 1999 test results. Tests 2 and 3 with the afterburner operating showed a nominal decrease in the emissions of SVOCs, but the decrease does not appear to be statistically significant.

Table 3-7. Semivolatile Organic Compound Emissions (g/kg initial wood)

Run	1	2	3	4
Phenol	6.43E-01	2.13E-01	3.97E-01	2.58E-02
2-Methylphenol	1.64E-01	6.67E-02	7.11E-02	5.17E-03
Acetophenone	1.96E-02	1.42E-02	1.09E-02	1.76E-03
4-Methylphenol	2.14E-01	7.50E-02	1.00E-01	9.64E-03
2,4-Dimethylphenol	5.61E-02	2.21E-02	2.01E-02	3.10E-03
Naphthalene	4.01E-01	2.00E-01	2.59E-01	1.21E-02
2-Nitrophenol	ND	ND	ND	2.58E-03
2-Methylnaphthalene	6.41E-02	3.33E-02	2.97E-02	1.48E-03
Acenaphthalene	1.10E-01	5.42E-02	5.85E-02	1.41E-03
1,4-Naphthoquinone	ND	ND	ND	1.65E-03
Acenaphthene	1.00E-02	5.42E-03	ND	ND
Dibenzofuran	3.89E-02	2.83E-02	2.97E-02	2.62E-03
4-Nitrophenol	ND	ND	ND	1.72E-03
Fluorene	2.72E-02	1.17E-02	1.09E-02	5.51E-04
Phenanthrene	9.62E-02	6.11E-02	6.69E-02	3.38E-03
Anthracene	1.48E-02	9.59E-03	8.78E-03	3.44E-04
Di-n-butyl phthalate	ND	ND	ND	4.48E-04
Fluoranthene	3.73E-02	2.58E-02	2.38E-02	1.55E-03
Pyrene	3.77E-02	1.75E-02	1.42E-02	1.24E-03
Benzo(a)anthracene	9.62E-03	5.00E-03	5.02E-03	ND
Chrysene	8.01E-03	5.42E-03	5.02E-03	ND
Benzo(b)fluoranthene	4.81E-03	3.25E-03	3.60E-03	ND

ND - none detected

3.9 Aldehyde Measurements

Table 3-8 lists the emissions of aldehydes from the various runs. There do not appear to be any trends in emissions of aldehydes whether or not the afterburner is operated. Note that, except for formaldehyde, emissions of most of the aldehydes are much lower than emissions of the VOCs and SVOCs. Formaldehyde emissions, however, are on the same order of magnitude as the benzene emissions.

Table 3-8. Aldehyde Emissions (g/kg initial wood)

Run	1	2	3	4
Formaldehyde	6.15E-01	3.36E-01	2.62E-01	5.09E-02
Acetaldehyde	1.25E-02	7.79E-03	7.48E-02	1.55E-02
Propanal	4.44E-03	ND	7.11E-03	3.47E-03
Benzaldehyde	5.29E-02	7.44E-02	2.52E-02	6.19E-03
Pentanal	3.07E-02	4.47E-02	8.38E-03	5.16E-02
Hexanal	1.48E-02	6.14E-03	5.97E-03	3.54E-03

ND - none detected

3.10 Methanol Measurements

Table 3-9 contains the methanol data. Methanol emissions were of the same order of magnitude as the aldehyde and benzene emissions. The methanol emissions were slightly lower than those reported in the 1999 report [Lemieux, 1999]. There doesn't appear to be any sort of noticeable trend with regards to the presence or absence of the afterburner.

Table 3-9. Methanol Emissions (g/kg initial wood)

Run	Methanol
1	1.29E-01
2	4.17E-01
3	1.57E-01
4	5.54E-02

3.11 Organic Compounds Found in Combustion Gases

Table 3-10 summarizes the data for the organic compounds as measured in the dilution tunnel. The data were collected for the final four burns after the system had been optimized.

Table 3-10. Concentrations of Organic Compounds (µg/m³)

Run	1	2	3	4
<u>Volatile Organic Compounds</u>				
1,4-Dichlorobenzene	1056	ND	ND	49
1,6-Dichlorobenzene	1648	ND	ND	66
Benzene	16,350	17,000	2369	47
Ethyl benzene	ND	101	ND	ND
Styrene	ND	174	224	ND
Toluene	2142	1732	285	ND
Xylenes	1763	51	ND	ND
<u>Oxygenated Compounds</u>				
2,4-Dimethylphenol	1040	130	90	14
2-Methylphenol	3060	400	320	23
4-Methylphenol	4000	450	450	43
Acetaldehyde	2	2	13	6
Acetophenone	365	85	50	8
Benzaldehyde	7	16	4	2
Formaldehyde	84	74	44	20
Hexanal	2	1	1	1
Methanol	541	2497	694	250
Pentanal	4	10	1	20
Phenol	12,000	1270	1770	120
Propanal	1	ND	1	1
<u>PAHs</u>				
2-Methylnaphthalene	1193	199	133	6.7
Acenaphthalene	2043	324	261	6.3
Acenaphthene	186	32	ND	ND
Anthracene	276	57	39	1.6
Benz[a]anthracene	179	30	22	ND
Benz[a]fluoranthene	90	20	16	ND
Chrysene	149	33	22	ND
Dibenzofuran	723	170	132	12
Fluoranthene	693	155	106	7
Fluorene	507	70	49	2.5
Naphthalene	7456	1198	1157	54
Phenanthrene	1789	365	299	15
Pyrene	701	104	67	6

ND – none detected

Table 3-11 is a list of aromatic compounds found in charcoal kiln smoke at measurable concentrations (in the dilution tunnel). The compounds have been sorted, with those found at the higher concentrations listed first. Some of the volatile and oxygenated compounds that might be related structurally or by common reaction mechanisms are also included.

Table 3-11. Identified Aromatic Compounds ($\mu\text{g}/\text{m}^3$)

Chemical	Chemical Formula	Molecular Weight	Approximate Concentration
Benzene	C_6H_6	78	17,000
Phenol	$\text{C}_6\text{H}_6\text{O}$	96	12,000
Naphthalene	C_{10}H_8	128	8,000
4-Methylphenol	$\text{C}_7\text{H}_9\text{O}$	109	4,000
2-Methylnaphthalene	$\text{C}_{11}\text{H}_{11}$	143	3,000
Toluene	C_7H_8	104	2,000
Xylenes	C_8H_{10}	106	2,000
Acenaphthalene	C_{12}H_8	152	2,000
Phenanthrene	$\text{C}_{14}\text{H}_{10}$	178	2,000
Dibenzofuran	$\text{C}_{12}\text{H}_8\text{O}$	168	700
Pyrene	$\text{C}_{16}\text{H}_{10}$	202	700
Fluoranthene	$\text{C}_{16}\text{H}_{10}$	202	700
Fluorene	$\text{C}_{13}\text{H}_{10}$	166	500
Anthracene	$\text{C}_{14}\text{H}_{10}$	178	300
Benz[a]anthracene	$\text{C}_{18}\text{H}_{12}$	228	200
Chrysene	$\text{C}_{18}\text{H}_{12}$	228	200
Acenaphthene	$\text{C}_{12}\text{H}_{10}$	154	200
Benz[a]fluoranthene	$\text{C}_{17}\text{H}_{10}$	216	100

4.0 CONCLUSIONS

4.1 General

Based on these simplified studies on the effect of an afterburner on emissions from Missouri-type charcoal kilns, it appears that, while the afterburner can offer significant benefits under some conditions, the operation of the afterburner is not a trivial matter. A system such as a charcoal kiln that relies on natural draft for operation may be upset by the addition of an afterburner due to pressure changes in the stack influencing the natural draft. Optimizing the process, both in the sense of good charcoal quality and good afterburner performance, may be difficult without the benefit of CEMs.

4.2 Conclusions from the Earlier Study That Were Confirmed by the Current Data

Conclusions formed after completion of the earlier [Lemieux, 1999] study and which were confirmed by the current data included the following:

- The wood used in these studies was representative of the wood used in commercial Missouri-type charcoal kilns.
- During a typical burn, the weight of the charcoal produced will be 20-30% of the weight of the wood used to produce the charcoal. Therefore, about 75% of the weight is lost as water, organic pollutants, or other materials.
- The combustion gases produced during a charcoal burn contain many different organic compounds. While many of these compounds appear to be products from chemical oxidation reactions, others are apparently from volatilization and from pyrolysis (see the partial list below).
- Phenols, aldehydes, acids, and PAH compounds were usually found in charcoal smoke. They were found in both the gaseous and solid phases.

When pyrolysis is used to manufacture charcoal from wood, many different organic compounds are released into the air depending on the specific pyrolysis or burn conditions. Table 4-1 lists those compounds found in the smoke of every burn tested to date. Other compounds found in the combustion gases of most burns would include all of the low molecular weight aldehydes, alcohols, acids and diacids, and several low-molecular-weight halogenated aliphatic and aromatic compounds.

Compounds found in most samples, along with an approximate upper concentration range, are shown in Table 4-1.

In addition to specific organic compounds, the concentration of THC's is usually above 5000 ppm and of the total PM is often above 20,000 $\mu\text{g}/\text{m}^3$ of air.

Table 4-1. Approximate Upper Concentration Ranges for Compounds as Measured in the Dilution Tunnel

Compound	Upper Concentration ($\mu\text{g}/\text{m}^3$)	Compound	Upper Concentration ($\mu\text{g}/\text{m}^3$)
Aldehydes & Ketones		PAHs	
Methanol	2500	Naphthalene	7500
Formaldehyde	100	Acenaphthalene	2000
Acetaldehyde	10	Phenanthrene	1800
Propanal	1	2-Methylnaphthalene	1200
VOCs		Dibenzofuran	720
Benzene	17,000	Pyrene	700
Toluene	2000	Fluoranthene	700
Xylenes	1800	Fluorene	500
Acetophenone	400	Anthracene	300
Styrene	200	Benz[a]anthracene	200
Ethylbenzene	100	Acenaphthene	200
SVOCs		Chrysene	150
Phenol	12000	Benz[a]fluorene	100
4-Methylphenol	4000		
2-Methylphenol	3000		
2,4-Dimethylphenol	3000		

4.3 Additional Conclusions from the Current Study

- The afterburner attached to the laboratory charcoal kiln simulator was difficult to operate to successfully create charcoal. The back pressure that the afterburner exerted on the system affected the natural draft of the kiln, impacting its ability to make charcoal. It is not known whether this conclusion will hold for a full-scale operation, but it is a concern. Based on the observations in this study, an afterburner that does not dramatically affect the natural draft of the system would be the most desirable retrofit for a full-scale charcoal kiln.
- Other pollutants such as aldehydes were produced during the charcoal manufacturing process. Emissions of aldehydes were somewhat less than emissions of VOCs, and on the same order of magnitude as emissions of PAHs.
- During a typical burn, the temperature increased for approximately 1 hour to about 700 °C where it peaked and then slowly decreased after the supply of oxygen was switched off.
- During a burn, the consumption of O₂ preceded the rise in temperature by 15-20 minutes. As the concentration of O₂ decreased, the concentration of all other combustion gases including CO, CO₂, NO, and THC increased. Typical concentrations at the time of the maximum kiln temperature were: O₂, 6%; CO₂, 13%; CO, 4%; NO, 100 ppm; and THC, over 5000 ppm.

- Even under laboratory conditions, the temperature readings throughout the kiln simulator were very uneven during most runs with the afterburner on, indicating that the process was not under control as well as we hoped for. It may be difficult to control the process in the field as a retrofit to existing charcoal kilns which may affect the quality of the charcoal produced.
- On average, 3.95 g of benzene is emitted for every 1 kg of wood fed into the simulator. On this basis, therefore, 633 lb of benzene would be released by 80 tons of wood.

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APPENDIX A: QUALITY CONTROL EVALUATION REPORT

General

When the kiln was initially lit, it was possible that the weigh scale was momentarily perturbed by the presence of the hand-held propane torch. When the flames or coals within the kiln were observed visually (as opposed to a smoke observation), it is also possible that the weight data record could show a momentary perturbation. These periods were brief.

Unless otherwise noted, assume that the standard afterburner operation procedure was to leave the afterburner air on throughout the test. The electronic ignitor and propane would be periodically switched on. Also assume that the ignitor was always activated when the propane was initially in use and generally switched off after a short period (when it was assumed that the afterburner flame would be self-sustaining). However, records of ignitor on/off cycles were not thorough.

During Run 1, the semivolatile train stopped early due to high vacuum, and the formaldehyde dry gas meter was improperly sized so the total volume for the formaldehyde sampling train was estimated from a constant rotameter reading of 0.5 scfh (0.24 L/min).

Flow Rate Measurements

Pitot traverses taken on August 26 and September 18 were consistent with each other and showed nearly consistent flow across the duct. Based on these pitot measurements, an average flow rate in the dilution tunnel was calculated to be 683 dscfm (19.3 m³/min).

CEM Data

The CEMs provided acceptable data quality for all runs.

Temperature Data

Certain thermocouples were not operational for some of the tests. Table A-1 lists the test days and the thermocouples which were not operational for those days.

Table A-1. Thermocouples That Were Non-Operational

Date	Non-Operational Thermocouples
8/21/98	TC40, TC41
8/25/98	TC33, TC40
8/28/98	TC33, TC40
9/2/98	TC33, TC36, TC40
9/3/98	TC33
9/10/98	TC33, TC40, TC41
9/14/98	TC33, TC40, TC41
9/16/98	TC33, TC40, TC41
9/18/98	TC33, TC40, TC41

Weight Data

Agreement between the amount of wood loaded, the measured charcoal production, and the observed weight loss is very poor. An independent balance was used to supplement the weight measurements. The main balance passed the quality control (QC) checks, but the QC checks did not simulate the heating or jarring that may have occurred during operation. It is likely that the weigh scale used to continuously measure the weight of the kiln was influenced by the high temperatures and possibly influenced by physical forces placed on the kiln system due to the afterburner and ignition equipment. Because of the weigh scale problems, independently measured weights of wood and charcoal were used.

VOC Measurements

A three-point calibration was performed prior to samples being analyzed on the Purge & Trap/GC/MS system. Three SUMMA canister standards were prepared at 10, 50, and 100 ppb. The standards were prepared by taking three cleaned, evacuated cylinders, adding 160 μ L of deionized water to each canister (to simulate sample conditions), adding 60, 300, and 600 mL of a 2 ppm gas to each of the three canisters, and filling each to a pressure of 2 atm with Ultra-Pure Carrier (UPC) grade air to get 10, 50, and 100 ppb gas standards, respectively. Portions (500 mL) for each of the three standards (and samples) were concentrated onto a Vocarb 3000 adsorbent trap (Purge & Trap) using a calibrated mass flow controller system. After 500 mL of standard/sample were concentrated, the adsorbent trap was dry-purged with helium for 10 minutes to reduce moisture, then rapidly heated to sweep the adsorbates onto the cryogenically cooled gas chromatography/mass spectrometry (GC/MS) system for analysis. Samples were quantified using the average response factor method across the calibration range. All target analytes had less than 30% standard deviation except for 1,4-dichlorobenzene and 1,2-dichlorobenzene for the initial calibration. A daily midpoint calibration check was performed prior to sample analysis. Relative percent deviations were quantified against the initial calibration curve and met the Method TO-14A guidelines for outlier allowances. A sample blank was analyzed prior to sample analysis each day. Of the four batch blanks that were performed, no target compounds were detected, except for trace amounts of chloromethane and toluene in one of the four blanks.

All samples had their pressures recorded after being logged. All samples were pressurized with UPC grade air to a final value of 2 atm pressure. The air flow rates used for filling the SUMMA canisters were calibrated using replicated Gilibrator gauge measurements and each canister was filled for a known amount of time at a known flow rate. Samples which had target analyte values exceeding the calibration range had less sample vacuum to get the exceeded value within the mid- and high-point of the calibration range. Sample multipliers were generated by calculating the total sample amount (volume determined using the ideal gas law using the pressure difference recorded on the Chain of Custody) plus the total amount of air added to pressurize the cylinder to 14.7 psig divided by the previously determined sample volume. Additional multipliers were added if less than 500 mL of sample was collected.

Sample concentrations were expressed in micrograms per cubic meter (nanograms per liter). Quantitation reports denote the nanogram amounts of each sample and are divided by the volume of sample pulled to report the samples in a weight/volume format. A method detection limit (MDL) study was not determined prior to the analyses; an estimated MDL of 2 ng for each target analyte was assigned. This value is about 10 % of the practical quantitation limit (PQL) for most target analytes in the list. Target analyte values which fell between the estimated MDL and PQL were reported, with the data flagged as below the calibration range. High target analyte concentrations for Tests 1, 2, and 4 limited the amount of sample pulled for these particular tests. This likely contributed to styrene's being reported as not detected in Test 1 because it fell just short of the MDL threshold.

SVOC Measurements

The samples when extracted were very dark. The first sample to be concentrated had material start to drop out of solution. Subsequent samples were not concentrated to the same point, but some material still dropped out upon cooling and storage. This indicates that concentrations possibly may be under reported.

All of the samples had a small portion filtered and internal standards added to the filtered portion. Therefore a large percentage aliquot of most samples has not been filtered.

The surrogate recoveries were acceptable for most samples. The blanks were very clean. The matrix spike recoveries were between 64 and 74% for naphthalene and between 82 and 98% for phenol. These two compounds were the only ones detected in significant concentrations. The recoveries for other mass spectrometer/mass selective detector compounds ranged from 64 to 148%. All of the compounds were spiked at 500 µg.

In the first four tests, the filter surrogates had very poor recovery. This was believed to be due to the spiking procedure where a filter is spiked and the solvent is allowed to dry. It is possible that this procedure resulted in the loss of some of the light surrogates.

Methanol Measurements

The data appear to show a significant concentration in the field blank. It is possible that contamination got into the sample either through methanol solvent usage in the laboratory or perhaps due to the burn hut's proximity to Interstate 40, where methanol may have been a component of automobile exhaust.

Aldehyde and Ketone Measurements

The aldehyde and ketone data passed all data quality criteria. The dry gas meter on Run 1 was oversized for the flow rate, so the sample volume on Run 1 was estimated based on the rotameter setting. An accuracy of $\pm 30\%$ is estimated for the rotameter flow rate.

PM Measurements

The data from the first test's sample should be largely discounted since over-tightening of the impactor led to the paper media's ripping, making it difficult to get accurate weights. Otherwise the data quality was acceptable. The flow rates were consistently somewhat above isokinetic, but the data analysis spreadsheet automatically adjusted the cutpoints of the various impactor stages to account for this.